Order-disorder transitions in comb-like polymer-surfactant systems involving hydrogen bonds

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ORDER - DISORDER TRANSITIONS IN COMB-LIKE POLYMER-SURFACTANT SYSTEMS INVOLVING HYDROGEN BONDS

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Abstract: Conditions to obtain micro-phase separated morphologies in polymer-surfactant systems involving hydrogen bonds have been investigated using poly(4-vinyl pyridine) (P4VP) and surfactants capable of forming hydrogen bonds of different strength with the basic nitrogen of P4VP. Depending on the tail length, the hydrogen bonding strength, the amount of surfactant and the temperature, four different regimes have been identified: I. Micro-phase separated state, II. Homogeneous state exhibiting a distinct Small Angle X-ray Scattering (SAXS) peak, III. Homogeneous state without a SAXS peak and, IV. Macro-phase separated state. Time-resolved SAXS / W(ide) A(angle) X(ray) S(cattering) / D(ifferential) S(canning) C(alorimetry) as well as rheological measurements are used to identify the different regimes. A simplified model description together with preliminary computer simulation results are presented.

INTRODUCTION

Flexible polymer-surfactant systems are situated on the borderline between classical microemulsions and conventional block copolymers. Our main interest concerns systems that can to a large extent be discussed in terms of familiar polymer physics concepts. Besides flexible polymers, relatively long chain surfactants are used, which contain a polar head interacting in a specific way with a complimentary group of the polymer. Poly(4-vinyl pyridine) with its basic nitrogen has been selected as an appropriate polymer capable of

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forming hydrogen bonds with various surfactants. Provided the tail of the surfactant is sufficiently long, i.e. of the order of several statistical segments, and the hydrogen bonding is sufficiently strong, complexes between the polymer and the surfactants molecules can be considered as comb-like copolymers and their properties can be described using the conventional Random Phase Approximation. As long as the concentration fluctuations are determined by the comb-like structures, the structure factor of the system, and hence the corresponding small angle scattering, will exhibit a peak at a finite value of the wave vector k. Only if the attractive interaction is so weak that the concentration fluctuations represent a homogeneous mixture of both components, will the peak disappear. In that case, macro phase separation may also occur.

MODEL AND COMPUTER SIMULATIONS

Fig. 1a illustrates hydrogen bonding between a typical representative of the above mentioned class of surfactants, pentadecyl phenol (PDP), with P4VP. Fig. 1b presents a simplified lattice model which is used in our computer simulation experiments (Ref. 1), and which comprises the essential concepts of polymer-surfactant systems involving hydrogen bonding.

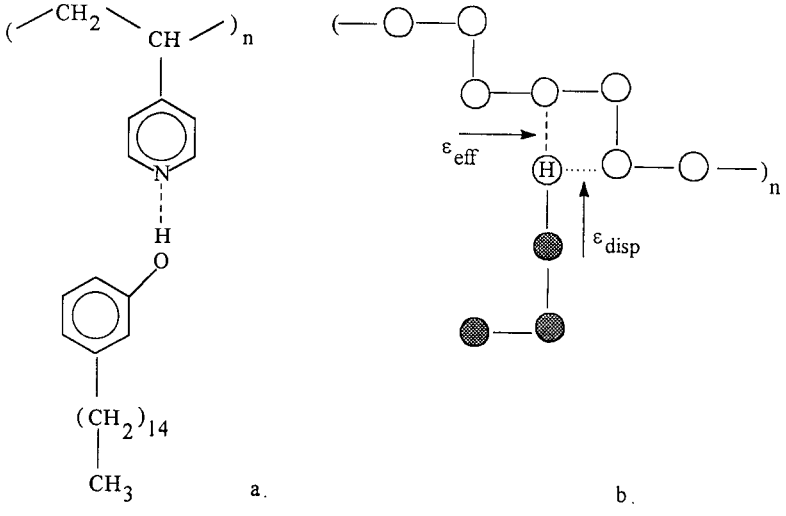

Fig. 1.a. P4VP-PDP hydrogen bond; b. Schematic lattice model: .... ε_{disp} , ---- ε_{eff} (see text).

It is very important to realize that unlike the ubiquitous dispersive forces, hydrogen bonding is extremely directional specific, i.e. in most instances two adjacent groups that can form a hydrogen bond will not be in the right spatial position to do so. The formation of a hydrogen bond is accompanied by a strong reduction in positional disorder, i.e. strong decrease in entropy. As a consequence, most hydrogen bonds will be replaced by dispersive forces at more elevated temperatures. This mechanism is at the basis of many experimentally observed closed loop phase diagrams of hydrogen bonding systems (Ref 2-4). The models used to describe these kind of systems are basically lattice models, with one additional feature taking the directional specific nature of the hydrogen bond into account. The following interactions can be distinguished:i. the hydrogen bonding energy between the two complimentary groups $\varepsilon_{hb}<0$, ii. the energy due to the dispersive forces if the two complimentary groups are not in the right position to form a hydrogen bond ε_{disp}, iii. the interaction between the segments of the surfactant tail and the polymer segments and iv. the interaction energy between the segments of the surfactant tail and the surfactant head. To introduce the directional specific nature of the hydrogen bond the following assumptions are made. First, only one hydrogen bond per polar group can be formed. This is accomplished by assuming that the surfactant head can make a hydrogen bond with a neighbouring polymer segment only if the latter is located in the direction of the bond connecting the head with its preceding tail "monomer" (Figure 1b presents an example, --- is a possible hydrogen bond). But even if a polymer segment and a surfactant head are in the right position with respect to each other, they do not necessarily form a hydrogen bond. To satisfy the requirement that at elevated temperatures the number of hydrogen bonds is strongly reduced a parameter q is introduced: if a polymer segment and a surfactant head are in a position with respect to each other which in principle allows a hydrogen bond to be formed, both groups involved have still so much freedom that out of $q+1$ "intrinsic" states only 1 corresponds to a hydrogen bond. In the past, this type of modeling has been applied successfully to hydrogen bonding systems (Ref 2-4). As a consequence, an effective hydrogen bonding interaction ε_{eff}, can be defined by

$$\varepsilon_{eff} = \lambda\varepsilon_{hb} + (1-\lambda)\varepsilon_{disp} \tag{1}$$

$$\lambda = \left(qe^{\beta\lambda\varepsilon} + 1\right)^{-1} \tag{2}$$

where $\Delta\varepsilon = \varepsilon_{hb} - \varepsilon_{disp}$ and $\beta = 1/kT$. Equation 2 represents the fraction of hydrogen bonds that are actually formed if the surfactant head and the polymer group are in a position where a hydrogen bond can be formed. As required, this fraction satisfies $\lambda << 1$ for $T \to \infty$, provided q>1 . Equation 1 implies a tendency of ε_{eff} to become less negative or even positive for elevated temperatures, where the dispersive interactions dominate. Figure 2 presents the structure factors obtained by preliminary computer simulations on a cubic lattice model under the following conditions: number of beads of polymer n = 32, number of beads of surfactant molecule m = 4, the volume fraction of polymers and surfactant molecules is equal and amounts to 0.4 (volume fraction of voids equals 0.2), all dispersive forces are equal and N = 64. For this specific case, Fig. 2 clearly demonstrates the development of a peak at finite wavelength for increasing hydrogen bonding attraction.

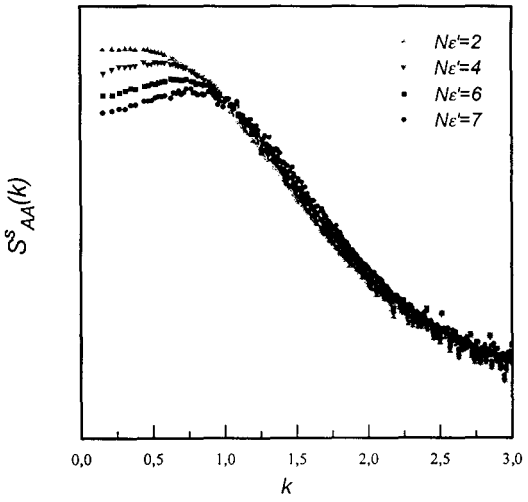

Fig.2. Structure factor of polymer/surfactant model. $\varepsilon' \equiv \varepsilon_{disp}/kT$; $\varepsilon'_{hb} \equiv \varepsilon_{hb}/kT = -20\varepsilon'$; q = 10.

EXPERIMENTAL RESULTS: REGIME I AND II

Regime I and II correspond to polymer-surfactant complexes behaving essentially like comb polymer molecules. Hence, this kind of situation corresponds to $\lambda \cong 1$ ($\Delta\varepsilon << 0$). Regime I corresponds to a micro phase separated state, whereas regime II represents a homogeneous state. The difference between both regimes is essentially a difference in polymer-surfactant tail

repulsion. Fourier Transform Infra Red (FTIR) measurements confirm that P4VP-PDP_x (x is the number of PDP molecules per pyridine group) systems satisfy $\lambda \cong 1$ as long as $x \leq 1$. For $x \geq 1$, the number of PDP molecules exceeds the number of pyridine groups and this excess will be present as free surfactant (Ref 5). Figure 3 presents time resolved SAXS of P4VP-$PDP_{0.85}$ during cooling with 5 °C/ min from the melt at 100 °C (Ref 6). Although a scattering peak at finite wavelength k^* is present right from the beginning, around 60 °C a strong increase is observed signalling the transition from a homogeneous disordered state to an ordered micro phase separated (lamellar) state. The DSC data taken simultaneously as well as separate optical microscopy observations (sample becoming birefringent) confirm this (Ref 6).

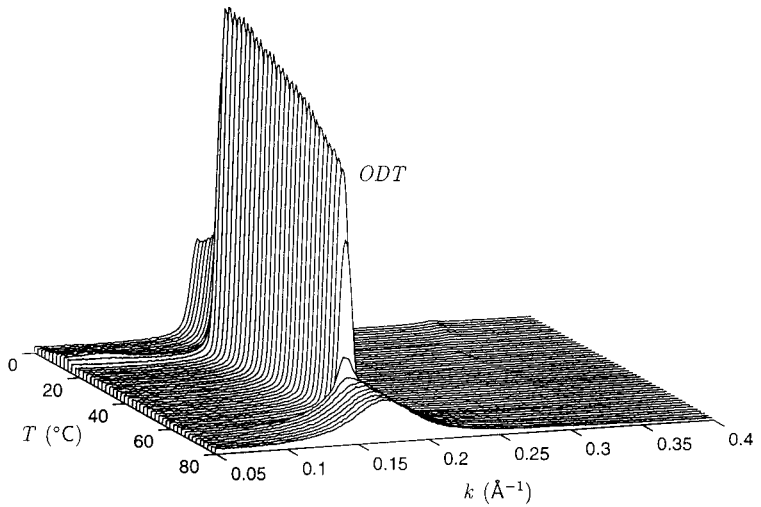

Fig. 3. Time resolved SAXS of P4VP-$PDP_{0.85}$

Order-disorder transitions in comb polymers have been discussed in length by Benoit and Hadziioannou (Ref 7). Assuming Gaussian statistics they showed that comb polymers micro phase separate for $\chi n > 10.5$, where $n = n_a + n_b$, n_a being the number of Kuhn segments of the main chain between two successive combs and n_b the number of Kuhn segments per comb; χ denotes the familiar Flory-Huggins parameter between main chain segments and comb segments. The order-disorder transition temperature for comb polymers is very sensitive

to the copolymer composition, i.e. the relative values of n_a and n_b. For P4VP-PDP_x, x denotes the number of PDP molecules per pyridine group and as such is a measure of the composition. The fact that an order-disorder transition has been found so far for values of $0.15 \leq x \leq 2.0$, shows that the repulsion between the tail of the surfactant and P4VP is rather strong. As noted above, this repulsion involves the product χn, underlining the importance of the length of the surfactant tail. For $x \geq 1$, we are actually dealing with a micro phase separated lamellar system in which the excess surfactant is dissolved in the surfactant layer.

As for ordinary block copolymers, the order-disorder also manifests itself in rheological measurements (Ref 8). Figure 4 presents a characteristic example of the dynamic elastic shear modulus G' as a function of frequency ω for various temperatures for P4VP-$PDP_{1.0}$ (Ref 9). Theoretically for di-block copolymer systems, $G' \propto \omega^{0.5}$ in the micro phase separated lamellar state and $G' \propto \omega^2$ in the homogeneous disordered state (Ref 8). Our data show a similar transition in scaling behaviour around 60 °C.

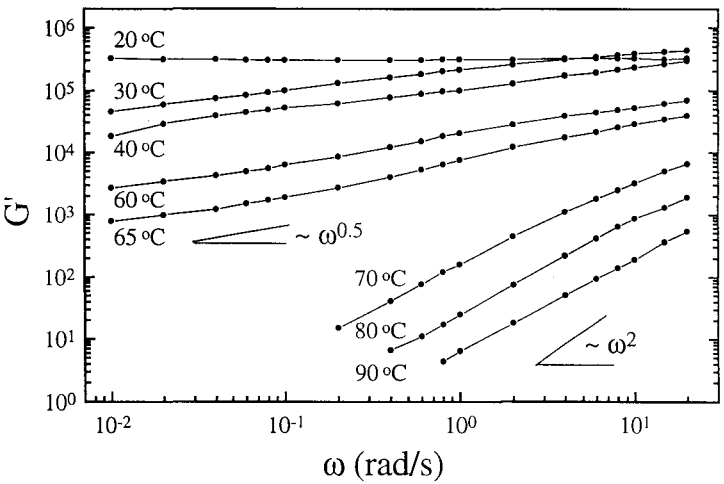

Fig. 4: Dynamic elastic shear modulus as a function of frequency for P4VP-$PDP_{1.0}$ near ODT.

The SAXS data show that the P4VP-PDP system is in a disordered state at 100 °C with a characteristic scattering peak. Hence, up to this temperature, hydrogen bonding is still the dominating interaction in the system. Theoretically, most of the hydrogen bonds will at more

elevated temperatures be replaced by the dispersive forces, in which case macro phase separation might occur. So far we have not seen any signs of macro phase separation at higher temperatures. However, even if the number of hydrogen bonds is strongly reduced and the dispersive forces dominate, this does not necessarily imply macro phase separation, since at these high temperatures the entropy of mixing may well become the driving force for miscibility. Still, compressibility effects will ultimately destabilize the system again (Ref 4). Clearly, it is of some interest to investigate the high temperature regime in more detail.

EXPERIMENTAL RESULTS: REGIME III

In the last section it was demonstrated that depending on the temperature the behaviour of P4VP with a typical phenol type surfactant can be classified as Regime I or II behaviour. Similar experiments with carboxylic surfactants (dodecanoic, hexadecanoic, etc) revealed a Regime II behaviour (Ref 10). Due to the strong crystallization tendency of the surfactants, an order-disorder transition upon cooling has not yet been observed. A more severe reduction in hydrogen bonding strength by taking aliphatic alcohol surfactants provides an example of Regime III, i.e. homogeneously mixed without a SAXS peak at nonzero wave vector. P4VP with dodecanol is a representative of this group and its SAXS pattern is shown in Fig. 5 (Ref 10). Apparently, the hydrogen bonding strength is too weak to introduce comb-like behavior.

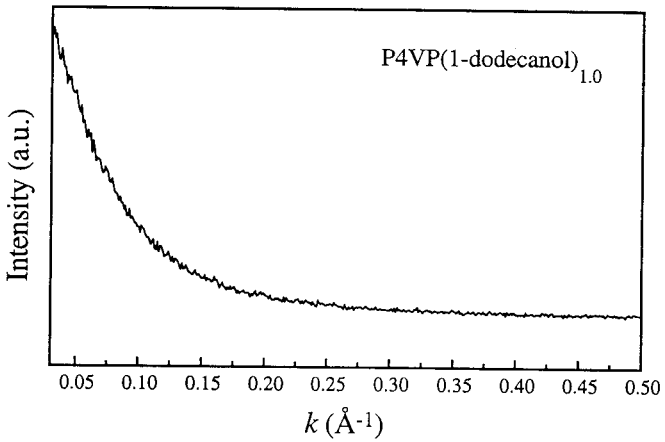

Fig. 5: SAXS of P4VP-dodecanol$_{1.0}$ at 60 °C.

EXPERIMENTAL RESULTS: REGIME IV

By increasing the tail length of the aliphatic alcohol surfactant the total repulsion energy in the system is increased above the critical value for macro phase separation and longer aliphatic alcohols therefore belong to regime IV (Ref 10).

CONCLUSIONS

Polymer-surfactant systems based on hydrogen bonding between the flexible polymer and surfactant are fascinating systems which combine the interesting phase behaviour of comb copolymers with time dependent aspects related to the hydrogen bonding equilibrium. The most obvious challenge now is to formulate a comprehensive theory to deal with these systems; a theory that contains the chemical equilibrium as one of its major ingredients.

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